

## PATENT SPECIFICATION

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## (54) POLYURETHANE ADHESIVE COMPOSITIONS

(71) We, TAKEDA YAKUHIN KOGYO KABUSHIKI KAISHA also known as TAKEDA CHEMICAL INDUSTRIES, LTD., a Japanese Company, of 27 Dosho-machi 2-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyurethane adhesive compositions which excel in such properties as adhesiveness and resistance to heat, water and chemicals.

Recently, m been develop packaging mat of two or more multi-layer cor purposes and factured by lat such material: polyethylene, terephthalate) nonwoven fab ide) or poly(vinylidene chloride); paper, synthetic paper, metal foils such as foils of aluminium or copper.

Bonding agents, such as polyurethanes, polyesters, polyamides, neoprene, poly(vinyl acetate), polyethylene and polyacrylate esters have been employed as laminating adhesives.

However, these adhesives are not fully satisfactory because of their deficiencies in adhesiveness and lack of resistance to aging, to water and to foils. For example, polyether polyurethane adhesives based on polyether polyols have good resistance to water but have poor adhesiveness and are especially lacking in initial tackiness and initial adhesiveness when applied to surfaces and, therefore, tend to cause the so-called "tunnelling" phenomenon in which the laminated films

become locally delaminated. On the other hand, polyester polyurethane adhesives have satisfactory adhesiveness but have poor water resistance. Especially those laminates which are used as sterilizable food packaging materials, which are subjected to sterilization with boiling water or high-pressure steam of about 130°C., must have an adequate degree of resistance to hot water. This desideratum precludes the use of polyester polyurethane adhesives in this field of application. The polyester polyols which are used in the production of polyester polyurethanes are prepared by the polycondensation reaction of a

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## ERRATUM

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21st March, 1977

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According to the present invention there is provided an adhesive composition comprising a mixture of (A) a polyurethane polyol obtained from an organic diisocyanate, a polyether polyester glycol and a polyol having 3 to 8 hydroxyl groups and a molecular weight not exceeding 400, and (B) an organic polyisocyanate, the ratio, excluding volatile solvents, of (A)/(B) being 100/1 to 100/100 by weight.

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The above-mentioned polyether polyester glycol may be prepared by reacting a polyether glycol, a dibasic acid anhydride and an alkylene oxide in the presence of a catalyst. Though the molecular weight of the polyether polyester glycol is largely optional, it is preferably 500 to 10,000, more preferably 500 to 4,000.

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This invention relates to polyurethane adhesive compositions which excel in such properties as adhesiveness and resistance to heat, water and chemicals.

Recently, multi-layer composite films have been developed for use especially as food packaging materials, the films being laminates of two or more dissimilar types of films. Thus, multi-layer composite films suitable for various purposes and applications have been manufactured by laminating in various combinations such materials as resin films, e.g. films of polyethylene, polypropylene, poly(ethylene terephthalate), nylon or regenerated cellulose; nonwoven fabrics of nylon, poly(vinyl chloride) or poly(vinylidene chloride); paper, synthetic paper, metal foils such as foils of aluminium or copper.

Bonding agents, such as polyurethanes, polyesters, polyamides, neoprene, poly(vinyl acetate), polyethylene and polyacrylate esters have been employed as laminating adhesives.

However, these adhesives are not fully satisfactory because of their deficiencies in adhesiveness and lack of resistance to aging, to water and to foils. For example, polyether polyurethane adhesives based on polyether polyols have good resistance to water but have poor adhesiveness and are especially lacking in initial tackiness and initial adhesiveness when applied to surfaces and, therefore, tend to cause the so-called "tunnelling" phenomenon in which the laminated films

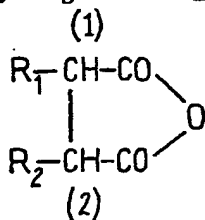
become locally delaminated. On the other hand, polyester polyurethane adhesives have satisfactory adhesiveness but have poor water resistance. Especially those laminates which are used as sterilizable food packaging materials, which are subjected to sterilization with boiling water or high-pressure steam of about 130°C., must have an adequate degree of resistance to hot water. This desideratum precludes the use of polyester polyurethane adhesives in this field of application. The polyester polyols which are used in the production of polyester polyurethanes are prepared by the polycondensation reaction of a dibasic acid with a polyhydric alcohol, and this reaction is conducted at a high temperature of 200 to 250°C, generally in a current of an inert gas, such as nitrogen or carbon dioxide. In this reaction, small amounts of aldehyde oxides are inevitably by-produced and their odour intermingles with the ester fragrance to impart a characteristic odour to the polyester polyols. Therefore, adhesives of this type are not suitable for food packaging applications.

According to the present invention there is provided an adhesive composition comprising a mixture of (A) a polyurethane polyol obtained from an organic diisocyanate, a polyether polyester glycol and a polyol having 3 to 8 hydroxyl groups and a molecular weight not exceeding 400, and (B) an organic polyisocyanate, the ratio, excluding volatile solvents, of (A)/(B) being 100/1 to 100/100 by weight.

The above-mentioned polyether polyester glycol may be prepared by reacting a polyether glycol, a dibasic acid anhydride and an alkylene oxide in the presence of a catalyst. Though the molecular weight of the polyether polyester glycol is largely optional, it is preferably 500 to 10,000, more preferably 500 to 4,000.

The polyether glycol may be any polyether glycol that is conventionally used as a starting material in the production of polyurethane resins and the molecular weight of the polyether glycol may be from 200 to 4,000, preferably from 200 to 2,000. For example, the polyether glycol may be obtained by the ring-opening addition polymerization reaction between an initiator having two active hydrogen atoms (e.g. ethylene glycol, propylene glycol, diethylene glycol or butylene glycol) and an alkylene oxide (e.g. ethylene oxide, propylene oxide or butylene oxide) or epichlorohydrin, or may be obtained by the ring-opening polymerization of tetrahydrofuran, oxacyclobutane or substituted oxacyclobutane.

The dibasic acid anhydride may be any conventional one, and is preferably an anhydride of a 1,2-dicarboxylic acid, which is represented by the general formula:



wherein  $R_1$  and  $R_2$  are the same or different, and each represent a hydrogen atom or a lower alkyl radical having 1 to 5 carbon atoms, or  $R_1$  and  $R_2$  may together with the carbon atoms at the (1) and (2)-positions, form part of a saturated or unsaturated ring having 6 to 12 carbon atoms which may be substituted by one or more halogen atoms (e.g. chlorine and bromine) or  $R_1$  and  $R_2$  may form a double bond between the carbon atoms at (1)-position and (2)-position. Examples of suitable dibasic acid anhydrides include maleic anhydride, succinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, 3,6-endomethylenetetrahydrophthalic anhydride, 3,6-endomethylenedichloromethylenetetrahydrophthalic anhydride and tetrabromophthalic anhydride. Of these anhydrides, maleic anhydride, succinic anhydride and phthalic anhydride are the most preferred. The alkylene oxide may for example be any of the compounds mentioned above, of which ethylene oxide, propylene oxide and mixtures thereof are preferred.

Examples of suitable catalysts which may be employed are alkali metal halides (e.g. sodium chloride and potassium chloride), alkali metal carbonates (e.g. sodium carbonate and potassium carbonate), zinc compounds (e.g. zinc phosphate and zinc oxide), ammonium halides (e.g. ammonium chloride and ammonium bromide), tertiary amines (e.g. N-methyl-morpholine, triethylamine and tri-

ethylenediamine) and dimethylformamide. While the catalyst may be used in substantially optional amounts, it is preferable to use 0.01 to 5.0 percent by weight of the catalyst relative to the reaction mixture.

In producing the polyether polyester glycol, the dibasic acid anhydride is used in the proportion of 1.2 to 20 moles, preferably 2 to 10 moles, per active hydrogen atom present in the polyether glycol and the alkylene oxide is used in an equimolar amount with respect to the dibasic acid anhydride. Satisfactory results are sometimes obtained when the ratio of the polyether and polyester segments which are formed in this step is controlled within the range of, by weight, 30:70 to 70:30. This reaction is generally carried out at a temperature of 70°C. to 200°C. and, for better results, at a temperature of from 100°C. to 150°C. Generally it is desirable to ensure that the sparging pressure will be zero to 3.0 kg./cm<sup>2</sup> gauge. Ordinarily, in conducting this reaction, the dibasic acid anhydride and catalyst are added to the polyether glycol and, then, the alkylene oxide is added. However, it is possible to follow a sequence in which the dibasic acid anhydride and catalyst are added to a mixture of the polyether glycol and alkylene oxide as the reaction progresses or a procedure in which the polyether glycol, dibasic acid anhydride, alkylene oxide and catalyst are all mixed together at one time and allowed to react. The foregoing procedures invariably give rise to a polyether polyester glycol consisting of a polyether segment to both ends of which polyester segments are attached. The polyether polyester glycol obtained above may be used also as a mixture with the polyether glycol mentioned above. In this case, however, the amount of the polyether glycol is less than 70 weight parts relative to 100 weight parts of the polyether polyester glycol.

The organic diisocyanate which is employed in the production of component (A) of the present adhesive composition is exemplified by hexamethylene diisocyanate, phenylene diisocyanate, 2,4- or 2,6- tolylene diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate,  $\omega,\omega'$ -diisocyanato-1,3-dimethylbenzene,  $\omega,\omega'$ -diisocyanato-1,4-dimethylbenzene,  $\omega,\omega'$ -diisocyanato-1,3-dimethylcyclohexene and  $\omega,\omega'$ -diisocyanato-1,4-dimethylcyclohexane, and various mixtures of such diisocyanates.

Examples of suitable polyols which contain 3 to 8 hydroxyl groups per molecule and which have a molecular weight of not more than 400 include triols such as glycerol, trimethylolpropane and 1,2,6-hexanetriol, and other polyols such as pentaerythritol, methyl

glucoside, xylitol, sorbitol and sucrose, the triols being preferred.

In the production of component (A), it should be noted that if a mixture of the polyether polyester glycol and polyol be reacted with an organic diisocyanate, the reaction mixture will undergo gelation. Therefore, it is recommended either to mix and react the polyether polyester glycol with the organic diisocyanate in such proportions as to provide an NCO/OH ratio of 1/1 to 2/1, preferably 1/1 to 1.2/1, to give an isocyanate terminated prepolymer and, then, react it with the low molecular weight polyol in such proportions as to provide an OH/NCO ratio of 2/1 to 20/1, preferably 4/1 to 10/1 or to mix and react, to some extent, the polyether polyester glycol with the organic diisocyanate in such proportions as to provide an NCO/OH ratio of 0.8/1 to 1/1 to give a mixture of an isocyanate-terminated prepolymer and polyether polyester glycol and then to add to the mixture the low molecular weight polyol in such proportions as to provide an OH/NCO ratio of 2/1 to 20/1, preferably 4/1 to 10/1.

The step leading to the formation of component (A) is ordinarily carried out at a reaction temperature of 50°C. to 100°C. This reaction may be conducted either in an organic solvent inert to the isocyanate, or in the absence of a solvent, although the use of a solvent is in certain instances conducive to more satisfactory results. In conducting the reaction, one may add a catalyst, for example, an organometallic compound such as dibutyltin dilaurate or stannous - 2 - ethylhexoate or a tertiary amine such as triethylenediamine, N-methylmorpholine or triethylamine, in an amount of 0.005 to 0.2 weight percent relative to reactant matter. Further, in order to increase the stability of the product one or more additives such as an antioxidant (e.g. 2,6 - di - t - butyl - 4 - methylphenol or 2,5 - di - t - butylhydroquinone), an ultraviolet absorber, a hydrolysis inhibitor (e.g. 3,3' - diisopropyl - 4,4' - biphenylenecarbodiimide) or an antifungal agent (e.g. 8 - hydroxyquinoline), may also be added in amounts not exceeding 5 percent relative to the reactant matter.

When the production of component (A) is carried out in the presence of an organic solvent, it is convenient to select the amount of solvent so that the reactant content of the final reaction mixture will be 5 to 90 weight percent and, preferably 20 to 75 weight percent.

The organic polyisocyanate used in component (B) is one having two or more NCO groups per molecule and may be either one of the organic diisocyanates usable for the production of component (A) or an organic triisocyanate such as 4,4',4'' - triphenylmethane isocyanate or tris(4 - isocyanophenyl) - thiophosphate. Furthermore the organic poly-

isocyanate may be obtained by reacting an excess amount of the said organic diisocyanate with a polyol having two or more OH groups. Examples of suitable polyols include diols such as ethylene glycol, diethylene glycol, 1,3 - butylene glycol, 1,4 - butylene glycol, 1,6 - hexanediol, cyclohexanediol, hydroquinonebis(hydroxyethylether), hydrogenated bisphenol and bis( $\beta$  - hydroxypropylether); triols such as glycerol, trimethylolpropane and 1,2,6 - hexanetriol; and other polyols such as pentaerythritol, methyl glucoside, xylitol, sorbitol and sucrose; the triols being preferred. In preparing the organic polyisocyanate from the organic diisocyanate and the polyol, the latter are allowed to react with each other in such amounts as to provide an NCO/OH ratio of, ordinarily, 1.5/1 to 10/1, preferably 1.7/1 to 5/1. Usually, this reaction is conducted at a temperature of 30°C. to 100°C. The reaction is carried out in the presence or absence of a solvent inert to the isocyanate, but it is generally desirable to employ a solvent. If desired, one may incorporate in the reaction system the above-mentioned organometallic catalyst, tertiary amine and other additives in amounts of 0.005 to 0.25 weight percent. It is also permissible, if desired, to cause allophanate bonds to be formed by the addition of a catalyst (e.g. stannous - 2 - ethylhexoate or triethylenediamine) or to cause biurets to be formed by the addition of a small amount of water or an amine (e.g. ethylenediamine or hexamethylenediamine). When a solvent inert to isocyanates is employed, it is expedient to ensure that the concentration of reactant matter in the resulting polyurethane polyisocyanate solution will be 5 to 90 weight percent and that the NCO content will be 5 to 25 weight percent.

Examples of the isocyanate-inert organic solvent which may be used as a reaction solvent in the production of the above component (A) or (B) include various esters, e.g. ethyl acetate, butyl acetate and 2-ethoxy ethanol acetate; ketones, e.g. acetone, methyl ethyl ketone, isobutyl ketone and cyclohexanone; ethers, e.g. tetrahydrofuran and dioxane; aromatic hydrocarbons, e.g. toluene and xylene; halogenated hydrocarbons, e.g. methylene chloride and ethylene chloride; dimethylsulphoxide; and dimethylsulphamide.

The present adhesive composition is manufactured by mixing the polyurethane polyol component (A) and organic polyisocyanate component (B), both of which can be produced in the above manner, in an (A)-to-(B) ratio (reactant matter in (A)/reactant matter in (B)) by weight of 100/1—100/100 or, for better results, 100/5—100/40. While the reactant matter content of the entire adhesive composition is virtually optional, it is more desirable, in terms of the convenience of use, to formulate the composition so that the reactant matter is 5 to 50 weight percent.

In actual bonding applications, the present adhesive composition is used in a conventional manner. Thus, for example, the composition may be applied to a surface or surfaces by roller coating or dipping and, after the solvent has evaporated, the surfaces are brought together. Then, the composition is cured at atmospheric temperature or under heating, preferably under the application of pressure.

As will be apparent from the experimental data to be given hereinafter, the present adhesive composition has excellent adhesiveness and resistance to heat, water and chemicals. Therefore, the present adhesive is useful as a bonding agent for packaging material films for drugs, food and other products (e.g. resin films such as films of polyethylene, polypropylene, poly(ethylene terephthalate), nylon, regenerated cellulose, polystyrene, poly(vinyl chloride) and poly(vinylidene chloride); synthetic papers of polystyrene and polyethylene; and metal foils such as foils of aluminium and copper).

The present invention is further explained by way of the following illustrative Examples and Experiment.

#### Example 1.

A reaction vessel fitted with a thermometer, propylene oxide inlet tube, stirrer, condenser and nitrogen inlet tube was charged with 250 parts by weight of polyoxypropylene glycol (molecular weight: 1000; OH number: 110 mg.KOH/g.), 157 parts by weight of maleic anhydride and 0.5 part by weight of N-ethylmorpholine and, under nitrogen sparging, propylene oxide (hereafter referred to sometimes as PO) was introduced by a volumetric pump. By the end of 30 minutes, appreciable heat had evolved to raise the temperature to 144°C., whereafter the reaction was allowed to proceed further at 120°C. The acid value dropped with the progress of the reaction until it was 0.1 mg.KOH/g. at the end of 8 hours. The reaction was then terminated, and the unreacted PO was distilled off, whereupon 500 parts by weight of reaction product were obtained. This product had an acid number of 0.1 mg.KOH/g., a hydroxyl number of 56.8 mg.KOH/g. and a molecular weight of 1980 (referred to as polyether polyester glycol-1). A solution comprising 396 parts by weight of above-prepared polyether polyester glycol, 36.6 parts by weight of tolylene diisocyanate (hereafter referred to sometimes as TDI) (2,4-/2,6-=80/20), 432.8 parts by weight of ethyl acetate and 0.22 part by weight of dibutyltin dilaurate catalyst was reacted at 60°C.—65°C. for 5 hours. When the viscosity of the reaction system at room temperature had reached 2000 cps., a mixture of 6.5 parts by weight of trimethylolpropane and 6.5 parts by weight of ethyl acetate was added and the reaction

was further allowed to proceed at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 2350 cps. (25°C.), referred to as Component A—I).

#### Example 2.

A solution comprising 396 parts by weight of polyether polyester glycol-1 prepared as in Example 1, 36.6 parts by weight of TDI (2,4-/2,6-=80/20), 432.8 g. of ethyl acetate and 0.22 part by weight of dibutyltin dilaurate catalyst was reacted at 60°C.—65°C. for 5 hours. When the viscosity of the reaction system at room temperature had reached 2,000 cps., a mixture of 6.5 parts by weight of 1,2,6-hexanetriol and 6.5 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 2400 cps. (25°C.), (referred to as Component A—II).

#### Example 3.

A reaction vessel fitted with attachments similar to those described in Example 1 was charged with 210 parts by weight of polyoxypropylene glycol (molecular weight 210), 182 parts by weight of maleic anhydride and 0.5 part by weight of N-ethylmorpholine, and heated at 120°C. With PO being introduced in the same manner as Example 1, the reaction was allowed to proceed for 5 hours, by the end of which time the acid number had dropped to 0.2 mg. KOH/g. The removal of volatile matter left 500 parts by weight of reaction product. This product had a molecular weight of 510 and a hydroxyl number of 110 mg. KOH/g., (referred to as Polyether polyester glycol-2).

A solution comprising 255.0 parts by weight of the above-prepared polyether polyester glycol-2, 91.5 parts by weight of tolylene diisocyanate (2,4-/2,6-=80/20), 346.7 parts by weight of ethyl acetate and 0.2 part by weight of dibutyltin dilaurate was reacted at 60°C.—65°C. for 7 hours. When the viscosity of the solution at 25°C. had reached 2500 cps., a mixture of 16.4 parts by weight of trimethylolpropane and 16.4 parts by weight of ethyl acetate was added and the reaction was further conducted at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 3000 cps. (25°C.) (referred to as Component A—III).

#### Example 4.

A reaction vessel fitted with attachments similar to those described in Example 1 was charged with 515 parts by weight of polyoxypropylene glycol (molecular weight 2060) 320 parts by weight of maleic anhydride and 1.0 part by weight of N-ethylmorpholine, and heated at 120°C. The reaction was carried out for 10 hours, PO being introduced in the same manner as Example 1. The reaction product

had an acid number of 0.3 mg. KOH/g. and a molecular weight of 4100 (referred to as Polyether polyester glycol-3).

5 A solution comprising 410.0 parts by weight of the above-prepared polyether polyester glycol-3, 18.3 parts by weight of tolylene diisocyanate (2,4-/2,6-=80/20), 428.5 parts by weight of ethyl acetate and 0.2 part by weight of dibutyltin dilaurate was reacted at 60°C.—65°C. for 5 hours. When the viscosity of the reaction system at room temperature had reached 4100 cps., a mixture of 3.3 parts by weight of trimethylolpropane and 3.3 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 5000 cps. (25°C.) (referred to as Component A—IV).

#### Example 5.

20 A solution comprising 396 parts by weight of polyether polyester glycol-1 prepared as in Example 1, 40.8 parts by weight of *ω,ω'*-diisocyanato - 1,3 - dimethyl - cyclohexane, 437 parts by weight of ethyl acetate and 0.22 part by weight of dibutyltin dilaurate catalyst was reacted at 60°C.—65°C. for 6 hours. When the viscosity of the reaction system at room temperature had reached 2,000 cps., a mixture of 6.6 parts by weight of trimethylolpropane and 6.6 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 2,400 cps. (25°C.), (referred to as Component A—V).

#### Example 6.

40 A reaction vessel fitted with attachments similar to those described in Example 1 was charged with 250 parts by weight of polyoxypropylene glycol (OH number: 112 mg. KOH/g.), 179.6 parts by weight of phthalic anhydride and 0.5 part by weight of N-ethylmorpholine, and heated at 120°C. under nitrogen sparging, propylene oxide being introduced by a volumetric pump. By the end of 30 minutes, appreciable heat had evolved. The reaction was allowed to proceed further at 120°C. The acid value dropped with the progress of the reaction until it was 0.15 mg. KOH/g. at the end of 9 hours. The reaction was then terminated, and the unreacted propylene oxide was distilled off, whereupon 500 parts by weight of reaction product were obtained. This product had an acid number of 0.15 mg. KOH/g., a hydroxyl number of 56.1 mg. KOH/g. and a molecular weight of 2,000 (referred to as Polyether polyester glycol-4).

60 A solution comprising 400 parts by weight of the polyether polyester glycol-4 obtained as above, 36.6 parts by weight of tolylene diisocyanate (2,4-/2,6-=80/20), 436.8 parts by weight of ethyl acetate and 0.2 part by

weight of dibutyltin dilaurate catalyst was reacted at 60°C.—65°C. for 5.5 hours. When the viscosity at room temperature had reached 2,000 cps., a mixture of 3.3 parts by weight of glycerol and 3.8 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 2,300 cps. (25°C.) (referred to as Component A—VI).

#### Example 7.

75 A solution comprising 400 parts by weight of polyether polyester glycol-4 prepared as in Example 6, 40.8 parts by weight of *ω,ω'*-diisocyanate - 1,3 - dimethyl benzene, 440.8 parts by weight of ethyl acetate and 0.1 part by weight of dibutyltin dilaurate was reacted at 60°C.—65°C. for 4 hours. When the viscosity of the reaction system at room temperature had reached 4,000 cps., a mixture of 3.8 parts by weight of glycerol and 3.8 parts by weight of ethyl acetate was added and the reaction was allowed to proceed at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 4,350 cps. (25°C.) (referred to as Component A—VII).

#### Example 8.

90 A solution comprising 400 parts by weight of polyether polyester glycol-4 prepared as in Example 6, 55.1 parts by weight of dicyclohexylmethane - 4,4' - diisocyanate, 455.5 parts by weight of ethyl acetate and 0.4 part by weight of stannous - 2 - ethyl - hexoate was reacted at 60°C.—65°C. When the viscosity of the reaction system at room temperature had reached 2,500 cps., a mixture of 3.8 parts by weight of glycerol and 3.8 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 2 hours. The resulting product had a viscosity of 2,800 cps (25°C.) (referred to as Component A—VIII).

#### Example 9.

110 A reaction vessel fitted with attachments similar to those described in Example 1 was charged with 500 parts by weight of polyoxypropylene glycol (OH number: 112 mg. KOH/g.), 316.2 parts by weight of succinic anhydride and 0.5 part by weight of N - ethyl - morpholine, and heated at 120°C. The reaction was carried out for 12 hours, propylene oxide being introduced in the same manner as Example 1. The reaction product had an acid number of 0.17 mg. KOH/g., a hydroxyl number of 58.1 mg. KOH/g. and a molecular weight of 1930 (referred to as Polyether polyester glycol-5).

125 A mixture of 386 parts by weight of polyether polyester glycol-5 prepared as above, 50.0 parts by weight of diphenylmethane - 4,4' - diisocyanate, 436.1 parts by weight of ethyl acetate and 0.1 part by weight of stan-

nous - 2 - ethylhexoate was reacted at 60°C.—65°C. When the viscosity of the reaction system at room temperature had reached 4,000 cps., a mixture of 5.4 parts by weight of trimethylolpropane and 5.4 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 2 hours. The resulting product had a viscosity of 4,300 cps. (25°C.) (referred to as Component A—IX).

#### Example 10.

A solution comprising 386 parts by weight of polyether polyester glycol-5 prepared as in Example 9, 38.8 parts by weight of  $\omega,\omega'$  - diisocyanate - 1,3 - dimethyl benzene, 424.9 parts by weight of ethyl acetate and 0.1 part by weight of dibutyltin dilaurate was reacted at 60°C.—65°C. When the viscosity of the reaction system at room temperature had reached 4,000 cps., a mixture of 5.4 parts by weight of trimethylolpropane and 5.4 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 2 hours. The resulting product had a viscosity of 4,400 cps. (25°C.) (referred to as Component A—X).

#### Example 11.

A solution comprising 386 parts by weight of polyether polyester glycol-5 prepared as in Example 9, 52.5 parts by weight of dicyclohexylmethane - 4,4' - diisocyanate, 438.5 parts by weight of ethyl acetate and 0.4 part by weight of stannous - 2 - ethylhexoate was reacted at 60°C.—65°C. When the viscosity of the reaction system at room temperature had reached 2,500 cps., a mixture of 5.4 parts by weight of trimethylolpropane and 5.4 parts by weight of ethyl acetate was added and the reaction was allowed to proceed further at 60°C.—65°C. for 1 hour. The resulting product had a viscosity of 2,700 cps. (25°C.) (referred to as Component A—XI).

#### Example 12.

A solution of 174.2 parts by weight of tolylene diisocyanate (2,4-/2,6=80/20) and 73.0 parts by weight of ethyl acetate was heated to 65°C. and 44.7 parts by weight of trimethylolpropane were added gradually. The reaction was allowed to proceed for 3 hours. The procedure yielded a polyurethane polyisocyanate having a reactant matter content of 75 weight % and an NCO content of 14.4 weight % (referred to as Component B—I).

#### Example 13.

A solution of 188.2 parts by weight of  $\omega,\omega'$  - diisocyanato - dimethyl - benzene and 77.6 parts by weight of ethyl acetate was heated to 65°C. and, then, 44.7 parts by weight of trimethylolpropane were gradually added. The mixture was allowed to react for 3 hours. The above procedure yielded a polyurethane polyisocyanate having a reactant matter content of 75 weight % and an NCO content of 13.5 weight % (referred to as Component B—II).

#### Example 14.

4,4',4'' - Triphenylmethane triisocyanate was dissolved in methylene chloride to give a 20% solution (referred to as Component B—III).

#### Example 15.

Tris(4 - isocyanophenyl)thiophosphate was dissolved in methylene chloride to give a 20% solution (referred to as Component B—IV).

#### Reference 1.

In the same manner as in Example 1, except that a polyoxypropylene glycol having a molecular weight of 2,000 was used in place of polyether polyester glycol-1, a polyurethane polyol component having a viscosity of 4,400 cps. (25°C.) and a reactant matter content of 50 weight % was prepared (referred to as Component a-I).

#### Reference 2.

In the same manner as in Example 1, except that a polyethylene adipate was used in place of the polyether polyester glycol-1, a polyurethane polyol component having a viscosity of 4,500 cps. (25°C.) and a reactant matter content of 50 weight % was prepared (referred to as Component a-II).

#### Example 16.

The polyurethane polyol components A—I, A—II, A—III, A—IV, A—V, A—VI, A—VII, A—VIII, A—IX, A—X, A—XI, a-I and a-II and polyurethane polyisocyanates B—I, B—II, B—III and B—IV, which are obtained by the procedures described in Examples 1 to 15 and References 1 and 2 were compounded in various combinations to prepare the following adhesive compositions (1) to (13). The compounding ratios are shown in Table 1.

TABLE 1 Formulations (parts by weight)

Component	Composition No.												
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
A-I	100												
A-II		100											
A-III			100										
A-IV				100									
A-V					100								
A-VI						100							
A-VII							100						
A-VIII								100					
A-IX									100				
A-X										100			
A-XI											100		
a-I												100	
a-II													100
B-I	4	4	4	4	6	4						4	4
B-II										6			
B-III							4				6		
B-IV								4	4				



## Experiment

The following adhesion tests were performed on the compositions (1) to (13) prepared in Example 16.

- 5 Polyethylene terephthalate films (hereafter sometimes referred to briefly as PET) (50  $\mu$  thick, "Diafoil" by Mitsubishi Resin Co., Ltd., Japan), polypropylene films (hereafter referred to as PP) (40  $\mu$  thick, "Torayfan" BO by Toray, Inc., Japan), polystyrene films (100  $\mu$  thick, "Styrosheet" # 500 by Asahi Dow Ltd.), or aluminium foils (hereafter referred to as Al) (30  $\mu$  thick, by Toyo Aluminium Co., Ltd., Japan) were coated with various adhesives, care being taken to ensure that the layers of adhesive were 10  $\mu$  thick, and, after preliminary drying, the adhesive surfaces were brought together and bonded at room temperature to 120°C. and a pressure of 5 kg./cm<sup>2</sup>.

The laminates were allowed to stand at

room temperature for 24 hours. Then, 15 mm. wide specimens were cut off and T-peel tests (ASTM-D-1876-69) or 180°-peel tests (ASTM-D-903-49) were performed on each sample on a "Tensilon" (Registered Trade Mark) testing machine at a jaw speed of 300 mm./min. Ten strips per sample were measured for each peel strength variable and the mean value was taken. In order to evaluate the resistance qualities of each laminate, a water resistance test was performed on specimens which had been immersed in water at 25°C. for 4 weeks; a chemical resistance test on specimens which had been immersed in a 4% aqueous solution of acetic acid at 25°C. for 4 weeks; and a heat resistance test on specimens which had been immersed in boiling water for 1 hour.

The results of these tests are set forth in Tables II, III and IV.

TABLE II T-Peel strength

Laminate	Adhesive composition	Peel strength g./1.5 cm.	Water resistance g./1.5 cm.	Chemical resistance g./1.5 cm.	Heat resistance g./1.5 cm.
Al-PET	(1)	630	600	580	630
	(2)	620	595	580	620
	(3)	520	525	530	550
	(4)	560	560	520	540
	(5)	800	780	750	810
	(6)	690	670	650	680
	(7)	750	740	750	760
	(8)	720	730	710	740
	(9)	640	650	630	620
	(10)	820	800	810	820
	(11)	740	730	720	740
	(12)	290	300	270	280
	(13)	635	360	290	345

TABLE III T-Peel strength

Laminate	Adhesive composition	Peel strength g./1.5 cm.	Water resistance g. 1.5 cm.	Chemical resistance g./1.5 cm.	Heat resistance g./1.5 cm.
Al-PP	(1)	605	610	580	610
	(2)	595	610	600	590
	(3)	530	530	520	540
	(4)	590	580	550	580
	(5)	860	830	800	840
	(6)	680	695	675	680
	(7)	740	720	730	760
	(8)	760	770	750	740
	(9)	650	640	650	630
	(10)	800	790	785	810
	(11)	710	720	700	690
	(12)	290	290	270	270
	(13)	600	350	310	300

TABLE IV 180°-Peel strength

Laminate	Adhesive composition	Peel strength g./1.5 cm.	Water resistance g./1.5 cm.	Chemical resistance g./1.5 cm.
PS-PP	(1)	560	570	580
	(2)	540	535	530
	(3)	490	475	480
	(4)	520	510	520
	(5)	680	690	670
	(6)	580	585	570
	(7)	670	665	660
	(8)	590	570	600
	(9)	530	510	515
	(10)	780	770	760
	(11)	580	575	565
	(12)	210	230	205
	(13)	340	180	170

(Heat resistance test was impossible because of deformation of PS-film by heat)

#### WHAT WE CLAIM IS:—

5 1. An adhesive composition comprising a mixture of (A) a polyurethane polyol obtained from an organic diisocyanate, a polyether polyester glycol and a polyol having 3 to 8 hydroxyl groups and a molecular weight not exceeding 400, and (B) an organic polyisocyanate, the ratio, excluding volatile solvents of (A)/(B) being 100/1 to 100/1000 by weight.

10 2. An adhesive composition as claimed in Claim 1, wherein the organic polyisocyanate is one having three NCO groups per molecule.

15 3. An adhesive composition as claimed in Claim 1 or 2, wherein the organic polyisocyanate is an adduct of tolylene-diisocyanate and trimethylolpropane.

20 4. An adhesive composition as claimed in any preceding claim, wherein the polyether polyester glycol is one having a molecular weight of 500 to 10,000.

25 5. An adhesive composition as claimed in any preceding claim, wherein the polyether polyester glycol is one having a molecular weight of 500 to 4,000.

6. An adhesive composition as claimed in any preceding claim, wherein the polyether polyester glycol is one prepared from a polyether glycol, a dibasic acid anhydride and an alkylene oxide.

7. An adhesive composition as claimed in any preceding claim, wherein the polyether polyester glycol is one prepared from polyoxypropylene glycol having a molecular weight of about 1,000, phthalic anhydride and propylene oxide.

8. An adhesive composition as claimed in any preceding claim, wherein the low molecular weight polyol is a triol.

9. An adhesive composition as claimed in any preceding claim, wherein the low molecular weight polyol is trimethylolpropane.

10. An adhesive composition as claimed in any preceding claim, wherein the ratio of (A)/(B) is 100/5 to 100/40 by weight.

11. An adhesive composition as claimed in any preceding claim, wherein the ratio of (A)/(B) is 10/1 by weight.

12. An adhesive composition substantially as hereinbefore described with reference to any one of Compositions 1 to 11 of Example 16 of the foregoing Examples.

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